**Supporting Information**

# Urea Degradation by Electrochemically Generated Reactive Chlorine Species: Degradation Products and Reaction Pathways

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**Quantification of Molar Flow Rate for Gas Products.** The m/z values of 14 and 44 were chosen as characteristic m/z for $N_2$ and $CO_2$, respectively. Potential interferences from $CO_2$, CO and $N_2O$ prohibited the ion intensity of m/z 14 to be used for $N_2$ quantification. Based on the negligible signal at m/z 30, an interference of $N_2O$ to the signal at m/z 44 was assumed to be marginal. The signal fraction of each characteristic m/z was calculated by the ratio to the sum of ion intensities (m/z 1 to 300). Based on the fragmentation profiles of standard $N_2$ and $CO_2$ provided by the supplier, the volume fractions were calculated by the following equations:

$$F_{N_2} = \frac{1080}{72} \frac{I_{14}}{\sum_{1}^{300} I_i} F_T \quad \text{(m/z 28:14:29 = 1000:72:8)} \qquad \text{(S1)}$$

$$F_{CO_2} = \frac{1199}{1000} \frac{I_{44}}{\sum_{1}^{300} I_i} F_T \quad \text{(m/z 44:28:16 = 1000:114:85)} \qquad \text{(S2)}$$

where, $I_i$ is ion intensity of fragment m/z $i$, while $F_{N2}$, $F_{CO2}$ and $F_T$ represent molar flow rate of $N_2$, $CO_2$, and total gaseous products, respectively. $F_T$ was calculated by converting the observed volumetric flow rate using ideal gas law, with considering conversion factors of the major gas components (1.4 for Ar, ca. 1 for $H_2$, $O_2$, $N_2$, $H_2O$).

$$F_T = \left( \frac{X_{Ar}}{1.4} + \frac{1 - X_{Ar}}{1} \right)^{-1} \frac{P}{RT} Q_{obs} \qquad \text{(S3)}$$

where, $X_{Ar}$ is the volumetric fraction of Ar, $Q_{obs}$ is the observed volumetric flow rate of total gaseous products, $P$ is the operational pressure (1 atm), $R$ is the gas constant, $T$ is the operational temperature (293 K).

**Measurement of Urea Concentration.** Figure S2 shows the evolution of the urea concentration under variable current density conditions, which was measured by urease hydrolysis method.[1] The measured urea concentration dropped off for the first sample under potential bias, whose further decrease was marginal. The required charge for the decrease in urea concentration for the initial 10 minutes exceeded the total passed charge even assuming one electron transfer for the urea transformation. The presence of reactive chlorine species (RCS), even with a trace concentration, would inhibit the activity of the enzyme urease.[2] In addition, the RCS was found to interfere in the spectrometric urea analysis by diacetylmonoxime.[3] The color generation by the reagent addition appeared to increase with the electrolysis time.

**Table S1.** The ohmic drop compensated anodic potential ($E_a - iR$) and current density ($J$) on average during the electrolysis of 41.6 mM urea solutions with 50 mM chloride (60 mM) under variable cell types and applied potentials ($E_a$).

| Cell Type | Electrolysis Time (h) | $E_a$ (V, NHE) | $E_a - iR$ (V, NHE) | $J$ (A $m^{-2}$) |
|---|---|---|---|---|
| Divided | 3 | 2.2 | 1.73 (3.1) | 23.8 (20) |
| | | 3.0 | 2.24 (4.7) | 83.3 (14) |
| Single Compartment | 6 | 3.0 | 2.05 (3.5) | 458 (7.5) |

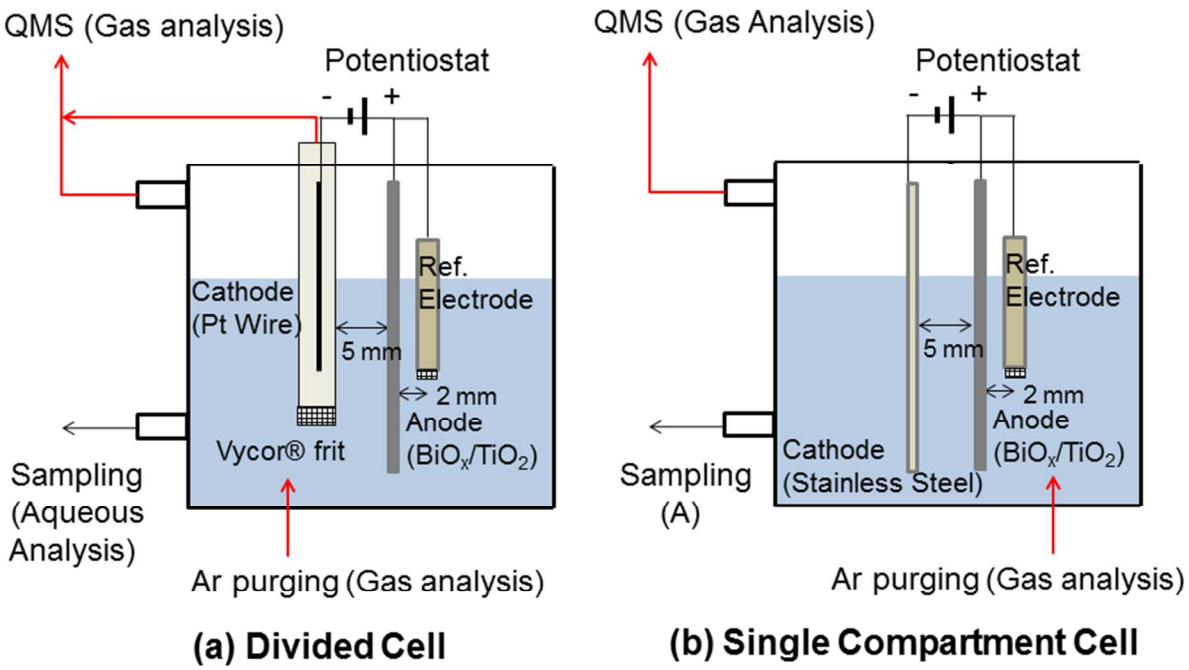


**Figure S1**. Schematic diagram of electrolysis cells (working volume: 60 mL) used in this study.

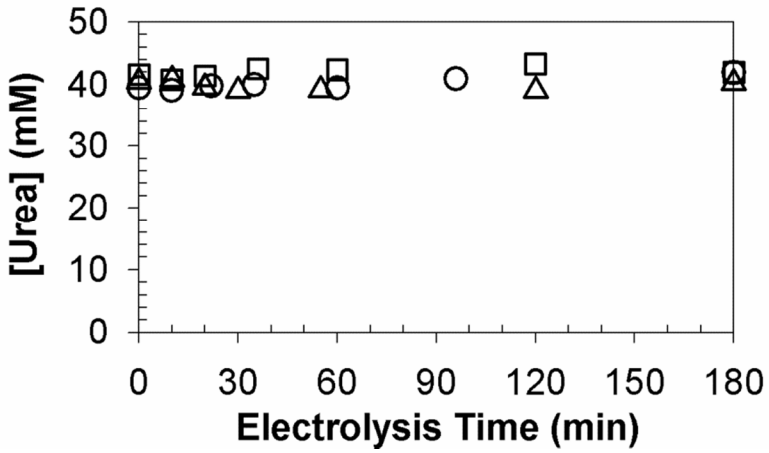


**Figure S2.** Time profiles of urea concentration during control electrolysis of 41.6 mM urea solutions in a divided cell; $E_a$: (circle) 2.2 V NHE with 50 mM $Na_2HPO_4$, (triangle) 3.0 V NHE with 50 mM $Na_2HPO_4$, (square) 1.3 V NHE with 50 mM NaCl, anode: $BiO_x/TiO_2$ (6 $cm^2$), cathode: Pt wire in frit separator.

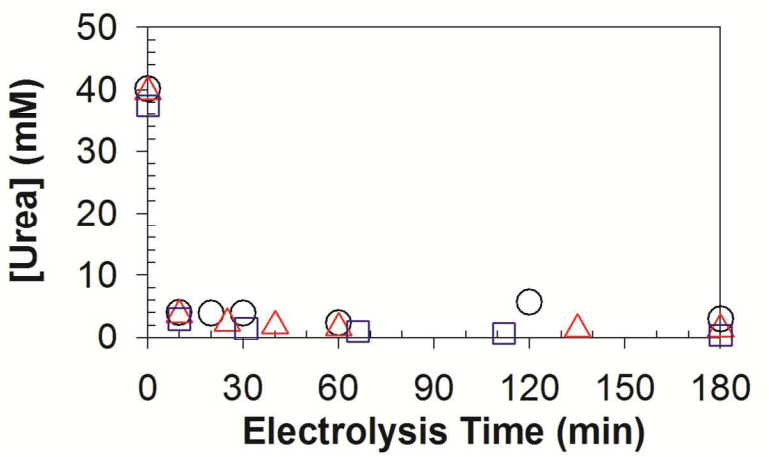


**Figure S3.** Time profiles of urea concentration during potentiostatic electrolysis of 41.6 mM urea solutions with 50 mM $Cl^-$ (60 mL); $E_a$: (circle) 2.2 V NHE in divided cell, (triangle) 3.0 V NHE in divided cell, (square) 3.0 V NHE in single compartment cell.

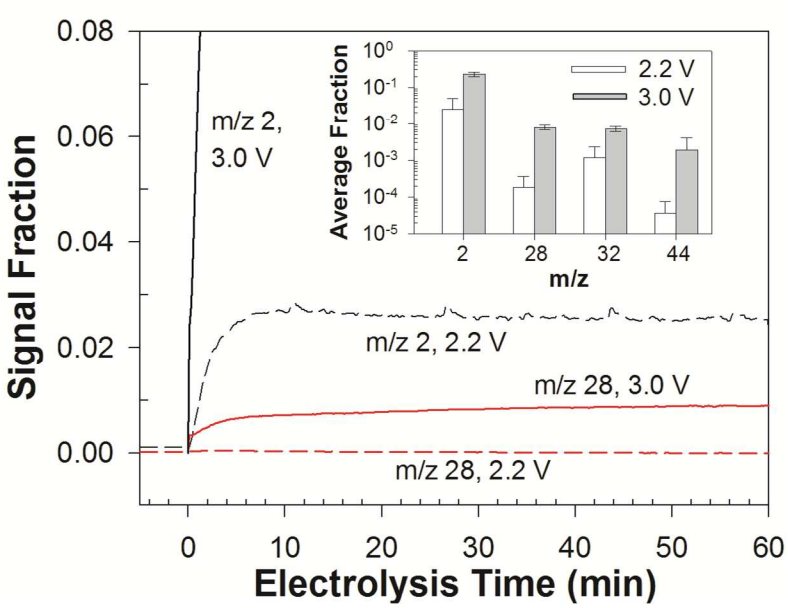


**Figure S4.** Time profiles of relative intensities for ion fragments m/z 2 and 28 in quadrupole mass spectrometer analysis during potentiostatic electrolysis of 41.6 mM urea solutions with 50 mM $Cl^-$ (60 mL) in divided cell; $E_a$: 2.2 V NHE (dashed line), 3.0 V NHE (solid line), anode: $BiO_x/TiO_2$ (6 $cm^2$), cathode: Pt wire in frit separator. Inset figure shows the relative intensities on average for ion fragments m/z 2, 28, 32, 44 for the initial 1 h.

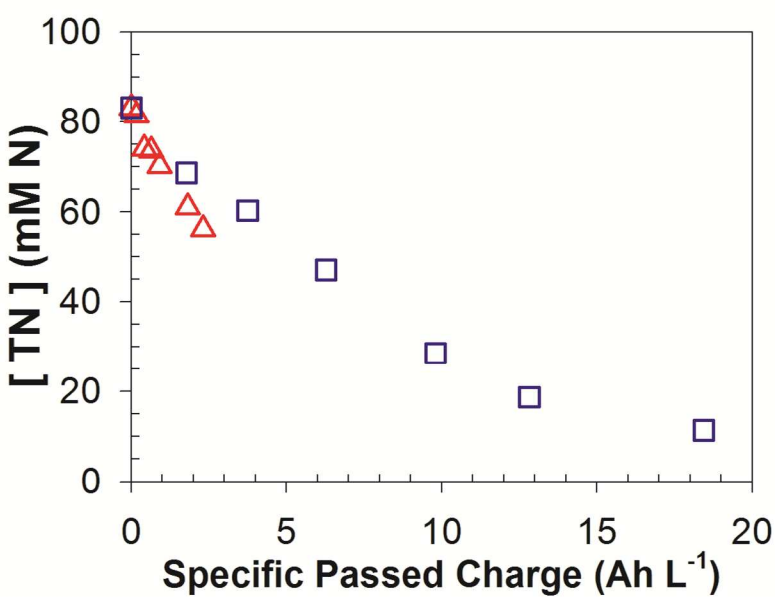


**Figure S5.** Total Nitrogen (TN) concentrations as functions of specific passed charges during potentiostatic electrolysis of 41.6 mM urea solutions with 50 mM $Cl^-$ (60 mL) in divided (triangle) and single compartment (square) cell; $E_a$: 3.0 V NHE, anode: $BiO_x/TiO_2$ (6 $cm^2$).

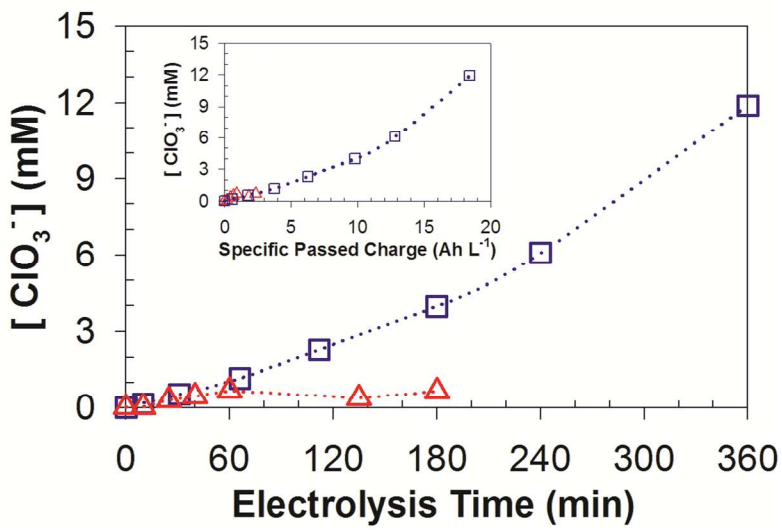


**Figure S6.** Evolutions of $ClO_3^-$ concentration as functions of electrolysis times and (inset) specific passed charges during potentiostatic electrolysis of 41.6 mM urea solutions with 50 mM $Cl^-$ (60 mL) in divided (triangle) and single compartment (square) cell; $E_a$: 3.0 V NHE, anode: $BiO_x/TiO_2$ (6 $cm^2$).

## REFERENCES

(1) Cho, K.; Kwon, D.; Hoffmann, M. R. Electrochemical treatment of human waste coupled with molecular hydrogen production. *RSC Adv.* **2014,** *4* (9), 4596-4608.

(2) Ikematsu, M.; Kaneda, K.; Iseki, M.; Yasuda, M. Electrochemical treatment of human urine for its storage and reuse as flush water. *Sci. Total Environ.* **2007,** *382* (1), 159-164.

(3) Prescott, L. M.; Jones, M. E. Modified Methods for Determination of Carbamyl Aspartate. *Anal. Biochem.* **1969,** *32* (3), 408-419.